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GLASSY CARBON BASED SUPERCAPACITOR STACKS

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Considerable effort is being made to develop electrochemical double layer capacitors (EDLC) that store relatively large quantities of electrical energy and possess at the same time a high power density. Our previous work has shown that glassy carbon is suitable as a material for capacitor electrodes concerning low resistance and high capacity requirements. We present the development of bipolar electrochemical glassy carbon capacitor stacks of up to 3 V. Bipolar stacks are an efficient way to meet the high voltage and high power density requirements for traction applications. Impedance and cyclic voltammogram measurements are reported here and show the frequency response of a 1, 2, and 3 V stack.

1 INTRODUCTION

Conventional electrolytic capacitors exhibit a very high specific power (W/kg) but quite low specific energy (Wh/kg). On the contrary, batteries feature high energy density, but they suffer from relatively low power density. For a wide spectrum of applications energy storage devices are needed which offer at the same time good energy and power density, i.e. energy systems which deliver within seconds several watt-hours of energy. These devices could be applied, for example, to provide peak power to load-level electric car batteries, as energy source for electrically heated catalysts or, in general, where intermittent high power is required.

Electrochemical double layer capacitors (EDLC), also known as supercapacitors or ultracapacitors (if pseudo-capacitance is included), seem to be very promising to meet the above mentioned energy and power requirements. The double layer arises primarily from the electrostatic interaction between electronic charge in the electrode phase and the ions and dipoles in the electrolyte phase. The larger the electrode/electrolyte interface the bigger the capacity to store electrical energy. Metal-oxides, doped conducting polymers, carbon or graphitic powder and, in our case, glassy carbon (GC) can be used as electrode materials.

A smooth glassy carbon surface has a double layer capacitance of about 20 μF/cm^2 (aqueous electrolyte). High capacitance is obtained when the surface is modified by electrochemical or chemical treatment in solution or air in a way that the effective surface increases by several orders of magnitude. Glassy carbon possesses the great advantage that the active layer, which makes up the very large double layer capacitance, forms a part of the current collecting electrode. Thus, contact resistance may be efficiently reduced.

2 BIPOLAR CONCEPT

The voltage of a unit cell capacitor comprised of two electrodes, which are activated on one side, is 1 or 3V depending on the electrolyte (aqueous or organic, respectively). In order to have several hundred volts, which are needed in some traction applications, the cells have to be connected in series either in a monopolar or bipolar way. The total resistance should be kept small so that the power density is optimized. For this reason, it is preferable to use the bipolar configuration in which bipolar electrodes, activated on both sides, are placed between two end plates activated only on one side (Figure 1). An ion conducting separator is used in order to avoid short current between the electrodes. It should be as thin and porous as possible so as to obtain a low separator resistance. Further, it must not be electronically conducting.

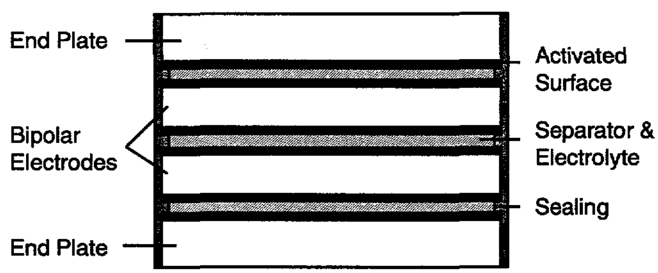

Fig. 1: View of a 3 cell capacitor stack with glassy carbon electrodes.

To avoid leakage currents on the periphery of the stack, it has to be sealed with an insulating seal to inhibit ionic and electronic contact from one cell to the other.

3 EXPERIMENTAL

The GC electrodes (19.64 cm^2, 5 cm Ø, 1 mm thick) were activated in air at 490 °C for one hour. Afterwards they were treated in 3 M H_2SO_4 and distilled water. Celgard® 3401 (25 μm thick) was used as separator and was soaked with 3 M H_2SO_4 before mounting. The impedance spectra as well as the cyclic voltammograms were measured with a EG&G potentiostat 273A in conjunction with a Solartron SI 1255 HF frequency response analyzer. The capacitance, C(ν), was calculated from the imaginary part of the impedance, Z(ν)":

$$C(\nu) = -1/(2\pi\nu Z(\nu)''). \qquad (1)$$

4 RESULTS AND DISCUSSION

One unit cell capacitor plus a two and a three volt capacitor stack were built. Figure 2 shows the cyclic voltammograms (CV) a), b) and c) of the three capacitors consisting of air activated GC electrodes. All CVs were measured with a scan rate of 10 mV/s. Curve a) shows the charging from 0 to 1 V with an average current of about 50 mA. The average charging currents for the 2 and 3 V stacks are 29 and 20 mA, respectively. Because of the series nature of the stack, the total capacitance is given by

$$1/C = \sum(1/C_i). \tag{2}$$

The capacitance of a capacitor is $C = Q/V$ (Q: charge, V: voltage). If Q is replaced by $I \cdot t$, then

$$C \cdot V = I \cdot t \tag{3}$$

(I: current, t: time). Based on eqs. (2) and (3) the current ratio is expected to be a):b):c) = 6:3:2 which is in good agreement with the measured values of b) and c). The product $C \cdot V$ corresponds to the integral under the CV curve and is, according to (3), the same in all three cases. The CV of an ideal capacitor would be a rectangle. Capacities which do not arise from a pure double layer and small leakage currents lead to a slight deviation of the CV curve from a rectangle.

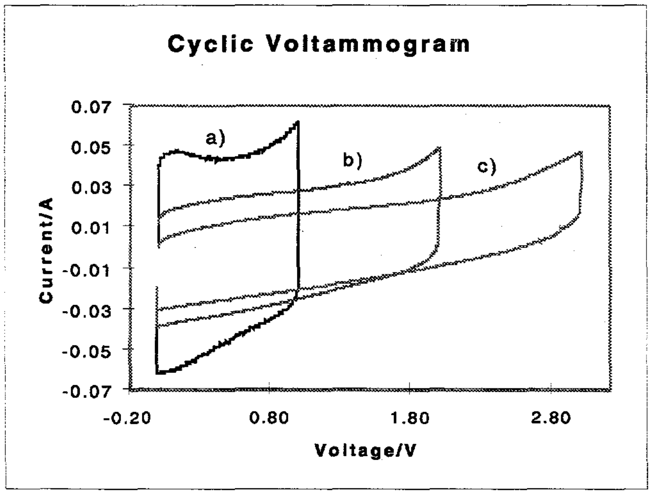

Fig. 2: Cyclic voltammograms of GC unit cell a), a 2 V, b), and a 3 V, c), capacitor stack. Scan rate 10 mV/s. Electrolyte is 3 M H_2SO_4.

The capacitance vs. frequency curves of the 1, 2, and 3 V 20 cm^2 capacitors are shown in Figure 3 and calculated as defined by eq. (1). The impedances were measured in each case with a fully charged capacitor. The capacities at 0.1 Hz are 2.9 F (1 V), 1.6 F (2 V), and 1.0 F (3 V). The value of 1.6 F is a bit smaller than the expected value of 2 F according to eq. 2. The capacitance decreases steadily with increasing frequency and is one order of magnitude smaller at 1000 Hz compared to 0.1 Hz. For an ideal capacitor, C is constant with frequency. However, for real capacitors, dispersion processes generally cause the value of C to decrease as the frequency increases. It is assumed that the formation of the electrochemical double layer is not complete at higher frequencies because of the limited mobility of the ions.

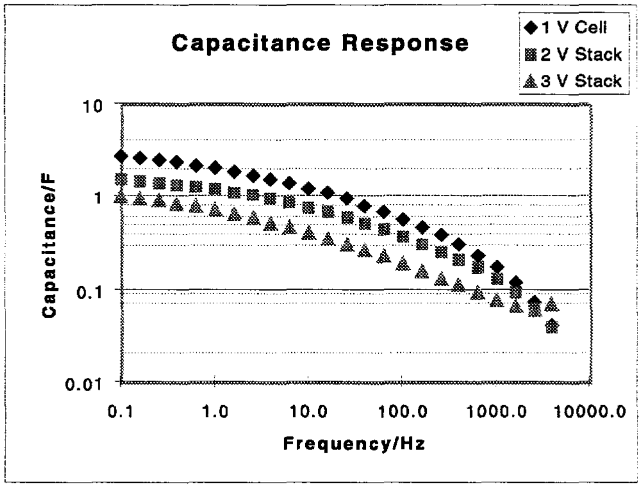

Fig. 3: Frequency dependence of the AC capacitance for the 1, 2 and 3 V capacitors.

5 CONCLUSIONS

Supercapacitors have the potential to deliver the energy and power that is needed in a variety of applications. After having succeded in building a unit cell capacitor with GC electrodes [1], we wanted to scale-up our device to a low voltage capacitor stack. The capacitance response of the 2 and 3 V stack corresponds to what would be expected based on the unit cell measurement. We could demonstrate a 3 V GC capacitor stack with air activated electrodes and 1 F capacitance. The fast activation in air seems to be a good alternative to electrochemical activation.

These initial results are quite promising, however, building even larger stacks with much higher voltages and lower total resistance still remains a big challenge.

6 ACKNOWLEDGMENTS

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7 REFERENCES

[1] M.G. Sullivan, M. Bärtsch, R. Kötz, O. Haas, ECS Meeting San Antonio, Texas, Meeting Abstracts, Vol. 96 (2), p. 845 (1996).